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Sertifikaat

REPUBLIEK VAN SUID AFRIKA



REPUBLIC OF SOUTH AFRICA

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PATENT OFFICE
DEPARTMENT OF TRADE AND
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the documents annexed hereto are true copies of:

Application forms P.1, P2 and provisional specification of South African Patent Application No. 2003/7774 as originally filed in the Republic of South Africa on 6 October 2003 in the name of SASOL TECHNOLOGY (PTY) LTD for invention entitled: "OLIGOMERISATION OF OLEFINS."

PRIORITY DOCUMENT
SUBMITTED OR TRANSMITTED IN
COMPLIANCE WITH
RULE 17.1(a) OR (b)

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PRETORIA

Signed at

in die Republiek van Suid-Afrika, hierdie
in the Republic of South Africa, this

17th dag van May 2004

day of

Registrar of Patents

REPUBLIC OF SOUTH AFRICA

PATENTS ACT, 1978

APPLICATION FOR A PATENT AND ACKNOWLEDGEMENT OF RECEIPT

[Section 30 (1) - Regulation 22]

Revenue stamps or revenue franking machine impression

Official date stamp

The grant of a patent is hereby requested by the undermentioned applicant on the basis of the present application filed in duplicate

OFFICIAL APPLICATION NO.

21 01 2003/7776

(i) APPLICANT'S OR AGENT'S REFERENCE
F491

(ii) FULL NAME(S) OF APPLICANT(S)

71 SASOL TECHNOLOGY (PTY) LTD

(iii) ADDRESS(ES) OF APPLICANT(S)

1 STURDEE AVENUE, ROSEBANK, 2196 JOHANNESBURG, SOUTH AFRICA

(iv) TITLE OF INVENTION

54 OLIGOMERISATION OF OLEFINS

(v) The applicant claims priority as set out on the accompanying form P2.

The earliest priority claimed is Country: Number: Date:

(vi) This application is for a patent of addition to Patent Application No.

21 01

(vii) This application is a fresh application in terms of section 37 and is based on Patent Application No.

21 01

(viii) This application is accompanied by:

1. A single copy of a provisional or two copies of a complete specification of 14 pages.

2. Drawings of sheets

3. Publication particulars and abstract (form P8 in duplicate).

4. A copy of Figure of the drawings for the abstract.

5. An assignment of invention.

6. Certified priority document(s) (state number):

7. Translation of the priority document(s).

8. An assignment of priority rights.

9. A copy of the form P2 and the specification of SA Patent Application No.

10. A declaration and power of attorney form P3.

11. Request for ante-dating on form P4.

12. Request for classification on form P9.

13. In terms of section 31(1) the applicant has added additional revenue stamps to this form for claiming priority after 12 months but before 15 months from the priority filing date.

14. Form P2 + copy

21 01

(ix) 74 Address for service: HAHN & HAHN INC, 222 Richard Street, HATFIELD, 0083, Pretoria

Dated this 6 day of October 2003

Plasa

Signature of applicant(s) or agent

This duplicate will be returned to the applicant's address for service as proof of lodging but is not valid unless endorsed with an official stamp

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REPUBLIC OF SOUTH AFRICA

FORM P2

PATENTS ACT, 1978

REGISTER OF PATENTS

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SASOL TECHNOLOGY (PTY) LTD

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|-------------------------------|-----------------|
| APPLICANTS SUBSTITUTED: 71 | DATE REGISTERED |
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| ASSIGNEE(S) 71 | DATE REGISTERED |
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| BLANN, Kevin; BOLLMANN, Annette; DIXON, John, Thomas; HESS, Fiona, Millicent; KILLIAN, Esna; MAUMELA, Hulisani; MORGAN, David, Hedley; NEVELING, Arno; OTTO, Stefanus | | | |
| PRIORITY CLAIMED NB - Use International abbreviation for country See Schedule 4) | COUNTRY 33 | NUMBER 31 | DATE 32 |
| TITLE OF INVENTION | | | |

OLIGOMERISATION OF OLEFINS

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| ADDRESS FOR SERVICE 4 HAHN & HAHN INC, PRETORIA | REF F491 |
| ENTITLEMENT OF ADDITION NO. | DATE OF ANY CHANGE |
| SEARCH APPLICATION BASED ON | DATE OF ANY CHANGE |

REPUBLIC OF SOUTH AFRICA
PATENTS ACT, 1978
PROVISIONAL SPECIFICATION
[Section 30(1) - Regulation 27]

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| FULL NAME(S) OF APPLICANT(S) | |
| SASOL TECHNOLOGY (PTY) LTD | |
| 71 | |

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|---|--|
| FULL NAME(S) OF INVENTOR(S) | |
| BLANN, Kevin; BOLLMANN, Annette; DIXON, John, Thomas; HESS, Fiona, Millicent; KILLIAN, Esna; MAUMELA, Hulisani; MORGAN, David, Hedley; NEVELING, Arno; OTTO, Stefanus | |
| 72 | |

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|----------------------------|--|
| TITLE OF INVENTION | |
| OLIGOMERISATION OF OLEFINS | |
| 54 | |

OLIGOMERISATION OF OLEFINS

Field of the invention:

This invention relates to the oligomerisation of ethylene. More particularly, the invention relates to a tetramerisation process, a catalyst system for tetramerisation of olefins and a ligand for a catalyst system for tetramerisation of olefins.

Background of the invention

This invention recognises the need for a catalyst system, which facilitates the production of 1-octene in high selectivity, while avoiding the co-production of significant quantities of butenes, other octene isomers, specific higher oligomers and polyethylene. The catalyst system can also be used for the tetramerisation of other olefins, especially α -olefins.

In this regard, it is known from prior art (US patent 6,184,428) that a nickel catalyst comprising a chelating ligand, preferably 2-diphenyl phosphino benzoic acid (DPPBA), a nickel precursor, preferably $\text{NiCl}_6 \cdot 6\text{H}_2\text{O}$, and a catalyst activator, preferably sodium tetraphenylborate, catalyse the oligomerisation of ethylene to yield a mixture of linear olefins containing considerable quantities of 1-octene. The selectivity towards linear C8 α -olefins is claimed to be 1.9%. Similarly, the Shell Higher Olefins Process (SHOP process, (US patents 3,676,523 and 3,635,937) using a similar catalyst system is reported to typically yield 11 mass % 1-octene in its product mixture (Chem Systems PERP reports 90-1, 93-6 and 94/95S12).

Similarly, Ziegler-type technologies based on trialkylaluminium catalysts, independently developed by Gulf (Chevron, e.g. DE patent 1,443,927) and Ethyl Corporation (BP/Amoco, e.g. US patent 3,906,053), are also commercially used

to oligomerise ethylene to mixtures of olefins that reportedly contain 13-25 mass % 1-octene (Chem Systems PERP reports 90-1, 93-6, and 94/95S12).

Moreover, chromium-based catalysts containing heteroatomic ligands with both phosphorous and nitrogen heteroatoms selectively catalyse the trimerisation of ethylene to 1-hexene. Examples of such heteroatomic ligands for ethylene trimerisation include bis-(2-diethylphosphino-ethyl)-amine (PCTZA02/00217) and (o-methoxy-phenyl)₂PN(Me)P(o-methoxy-phenyl)₂ (WO 02/04119). Since these catalyst systems are very specific for the production of 1-hexene, they only yield 1-octene as an impurity (typically less than 3 mass % of the product mixture as disclosed by WO 02/04119).

Summary of the invention

This invention generally relates to how the need for selectively producing 1-octene from ethylene can be satisfied by using a transition metal catalyst system containing a heteroatomic ligand.

Thus, according to a first aspect of the invention there is provided a process for the tetramerisation of ethylene, the process including the step of contacting the ethylene with a catalyst system which includes a heteroatomic ligand and a transition metal precursor.

The term "tetramerisation" generally refers to the reaction of four ethylene units to yield a linear olefin.

By heteroatomic is meant a ligand that contains at least two heteroatoms, which can be the same or different, where the heteroatoms may be selected from phosphorus, arsenic, antimony, oxygen, sulphur or nitrogen. More specifically the ligand may be described by the following general formula: (R¹)(R²)A-B-C(R³)(R⁴), where A and C are independently phosphorus, arsenic, antimony, oxygen,

sulphur or nitrogen and B is a linking group between A and C. A and/ or C may be a potential donor site.

B may be any linking group, for example hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl or substituted heterohydrocarbyl linking groups, or inorganic linking groups, including single atom links such as -B-, -O- and -S-. B may optionally contain any additional potential donor site. Examples of B include methylene, 1,2-ethane, 1,2-phenylene, 1,2-propane, 1,2-catechol, 1,2-dimethylhydrazine, $-\text{Si}(\text{CH}_3)_2-$, $-\text{N}(\text{R}^5)$ where R^5 is hydrogen, a hydrocarbyl or substituted hydrocarbyl, a substituted heteroatom (including silicon), a halogen, and the like. B may preferably be $-\text{N}(\text{R}^5)$ and R^5 may be a hydrocarbyl or substituted hydrocarbyl.

A and C may be phosphorus.

R^1 , R^2 , R^3 and R^4 are each independently hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl or substituted heterohydrocarbyl groups. Suitable examples of R^1 , R^2 , R^3 and R^4 include, but are not limited to, methyl, ethyl, ethylenyl, propyl, butyl, cyclohexyl, benzyl, phenyl, tolyl, xylyl, mesityl, biphenyl, naphthyl, anthracenyl, methoxy, ethoxy, phenoxy, tolyloxy, dimethylamino, thiomethyl, thiophenyl, trimethylsilyl, dimethylhydrazyl and the like. Preferably, R^1 , R^2 , R^3 and R^4 are independently substituted aromatic groups and the substituent is a polar group, on the meta- and/ or para-positions.

Any of the groups R^1 , R^2 , R^3 and R^4 may independently be linked to one or more of each other or to the linking group B to form a cyclic structure together with A and C, A and B or B and C.

The ligands can be prepared using procedures known to one skilled in the art and disclosed in published literature. Examples of ligands are: $(3\text{-methoxyphenyl})_2\text{PN}(\text{methyl})\text{P}(3\text{-methoxyphenyl})_2$ and $(4\text{-}$

$\text{methoxyphenyl}_2\text{PN}(\text{methyl})\text{P(4-methoxyphenyl)}_2$ and (3-
 $\text{methoxyphenyl}_2\text{PN}(\text{isopropyl})\text{P(3-methoxyphenyl)}_2$ and (4-
 $\text{methoxyphenyl}_2\text{PN}(\text{isopropyl})\text{P(4-methoxyphenyl)}_2$ and (4-
 $\text{methoxyphenyl}_2\text{PN}(2\text{-ethylhexyl})\text{P(4-methoxyphenyl)}_2$.

The process may be a process for tetramerisation of α -olefins.

The process may be a process for tetramerisation of ethylene.

The process may include the step of combining a heteroatomic ligand with a transition metal precursor and an activator.

The transition metal may be selected from chromium, molybdenum, tungsten, titanium and zirconium. Preferably, the transition metal is chromium.

The transition metal precursor which, upon mixing with the heteroatomic ligand and an activator, catalyses ethylene tetramerisation in accordance with the invention, may be simple inorganic and organic salts, for example halides, acetylacetones, carboxylates, oxides, nitrates, sulfates and the like, as well as co-ordination and organometallic complexes, for example, chromium trichloride tris-tetrahydrofuran complex, (benzene)tricarbonyl chromium, chromium hexacarbonyl, molybdenum hexacarbonyl and the like. The preferred transition metal precursors are chromium (III) acetylacetone and chromium (III) tris-2-ethylhexanoate.

The process may include the step of adding a coordination complex of a heteroatomic ligand and a transition metal precursor to a reaction mixture, or the step of adding separately to the reactor, a heteroatomic ligand and a transition metal precursor such that a heteroatomic coordination complex of a transition metal is generated *in-situ*. Typically, the heteroatomic coordination complex is generated *in-situ*. The transition metal precursor, and heteroatomic ligand are

combined (both *in-situ* and *ex-situ*) to typically provide metal/ligand ratios from about 0.01:100 to 10 000:1, and preferably, from about 0.1:1 to 10:1. The heteroatomic ligand may also be formed *in-situ*, for example by the reduction of a phosphine oxide to phosphine.

The heteroatomic ligand can be modified to be attached to a polymer chain (molecular wt. = 1000 or higher) so that the resulting heteroatomic coordination complex of the transition metal is soluble at elevated temperatures, but becomes insoluble at 25°C. This approach would enable the recovery of the complex from the reaction mixture for reuse and has been used for other catalyst as described by D.E. Bergbreiter *et al.*, *J. Am. Chem. Soc.*, 1987, **109**, 177-179. In a similar vein these transition metal complexes can also be immobilised by binding the heteroatomic ligands to silica, silica gel, polysiloxane or alumina backbone as demonstrated by C. Yuanyin *et al.*, *Chinese J. React. Pol.*, 1992, **1**(2), 152-159 for immobilising platinum complexes.

The activator for use in the process may in principle be any compound that generates an active catalyst when combined with the heteroatomic ligand and the transition metal precursor. Mixtures of activators may also be used. Suitable compounds include organoaluminium compounds, organoboron compounds, organic salts, such as methyl lithium and methyl magnesium bromide, inorganic acids and salts, such as tetrafluoroboric acid etherate, silver tetrafluoroborate, sodium hexafluoroantimonate and the like.

Suitable organoaluminium compounds include compounds of the formula AlR_3 , where each R is independently $\text{C}_1\text{-C}_{12}$ alkyl, oxygen or halide, and compounds such as LiAlH_4 and the like. Examples include trimethylaluminium (TMA), triethylaluminium (TEA), tri-isobutylaluminium (TIBA), tri-*n*-octylaluminium, methylaluminium dichloride, ethylaluminium dichloride, dimethylaluminium chloride, diethylaluminium chloride, aluminium isopropoxide, ethylaluminumsesquichloride, methylaluminumsesquichloride, and alumoxanes.

Alumoxanes are well known in the art as typically oligomeric compounds which can be prepared by the controlled addition of water to an alkylaluminium compound, for example trimethylaluminium. Such compounds can be linear, cyclic, cages or mixtures thereof. Mixtures of different aluminoxanes may also be used in the process.

Examples of suitable organoboron compounds are boroxines, NaBH₄, triethylborane, tris(pentafluoropheny)borane, tributyl borate and the like.

The activator may also be or contain a compound that acts as a reducing or oxidising agent, such as sodium or zinc metal and the like, or oxygen and the like.

The activator may be selected from aluminoxanes including alkylaluminoxanes such as methylaluminoxane (MAO), ethylaluminoxane (EOA), hexylaluminoxane (HAO) and modified alkylaluminoxanes such as modified methylaluminoxane (MMAO).

The transition metal, as the precursor or a heteroatomic coordination complex, and the aluminoxane may be combined in proportions to provide Al/metal ratios from about 1:1 to 10 000:1, and preferably, from about 1:1 to 1000:1.

The process may include the step of adding to the reaction mixture a trialkylaluminium compound in amounts of between 0.01 to 1000 mol per mol of aluminoxane. It should however be noted that aluminoxanes generally also contain considerable quantities of the corresponding trialkylaluminium compounds used in their preparation. The presence of these trialkylaluminium compounds in aluminoxanes can be attributed to their incomplete hydrolysis with water. Any quantity of a trialkylaluminium compound quoted in this disclosure is additional to alkylaluminium compounds contained within the aluminoxanes.

The individual components of the catalyst system described herein may be combined simultaneously or sequentially in any order, and in the presence or absence of a solvent, in order to give an active catalyst. The mixing of the catalyst components can be conducted at any temperature between -100°C and 200°C. The presence of an olefin during the mixing of the catalyst components generally provides a protective effect which may result in improved catalyst performance.

The catalyst system, in accordance with the invention, or its individual components, may also be immobilised by supporting it on a support material, for example, silica, alumina, MgCl₂, zirconia, natural clay, artificial clay or mixtures thereof, or on a polymer, for example polyethylene, polypropylene, polystyrene, or poly(aminostyrene). The catalyst can be formed in-situ in the presence of the support material, or the support can be pre-impregnated or premixed, simultaneously or sequentially, with one or more of the catalyst components. In some cases, the support material can also act as or as a component of the activator. This approach would also facilitate the recovery of the catalyst from the reaction mixture for reuse. The concept was successfully demonstrated with a chromium-based ethylene trimerisation catalyst by T. Monoi and Y. Sasaki, *J. Mol. Cat.A:Chem.*, 1987, 109, 177-179. In some cases, the support can also act as a catalyst component, for example where such supports contain aluminoxane functionalities or where the support is capable of performing similar chemical functions as an aluminoxane, which is for instance the case with IOLA™ (a commercial product from GRACE Davison Catalysts).

The reaction products, or in other words olefin oligomers, as described herein, may be prepared with the disclosed catalyst system by homogeneous liquid phase reaction in the presence or absence of an inert solvent, and/or by slurry reaction where the catalyst system is in a form that displays little or no solubility, and/or a two-phase liquid/liquid reaction, and/or a bulk phase reaction in which

neat reagent and/or product olefins serve as the dominant medium, and/or gas phase reaction, using conventional equipment and contacting techniques.

The process may therefore also be carried out in an inert solvent. Any inert solvent that does not react with the activator can be used. These inert solvents may include any saturated aliphatic and unsaturated aliphatic and aromatic hydrocarbon and halogenated hydrocarbon. Typical solvents include, but are not limited to, benzene, toluene, xylene, cumene, ethylbenzene, diethylbenzene, hexane, heptane, cyclohexane, octane, octene and the like. Particularly preferred solvents are toluene and cumene.

The process may be carried out at pressures from atmospheric to 150 barg. Ethylene pressures in the range of 10-70 bar are preferred. Particularly preferred pressures range from 30-50 barg.

The process may be carried out at temperatures from -100 °C to 250 °C. Temperatures in the range of 0-130 °C are preferred. Particularly preferred temperatures range from 35-100°C.

In a preferred embodiment of the invention, the catalyst system and reaction conditions are selected such that the yield of 1-octene from ethylene is greater than 25 mass %, preferably greater than 35 mass %. In this regard yield refers to grams of 1-octene formed per 100g of total reaction product formed.

Although the catalysts, its individual components, reagents, solvents and reaction products are generally employed on a once-through basis, any of these materials can, and are indeed preferred to, be recycled to some extent in order to minimise production costs.

The process may be carried out in a plant which includes any type of reactor. Examples of such reactors include, but are not limited to, batch reactors, semi-

batch reactors and continuous reactors. The plant may include, in combination a) a reactor, b) at least one inlet line into this reactor for olefin reactant and the catalyst system, c) effluent lines from this reactor for oligomerisation reaction products, and d) at least one separator to separate the desired oligomerisation reaction products, wherein the catalyst system may include a heteroatomic coordination complex of a transition metal salt and an activator, as described herein.

In another embodiment of the process the reactor and a separator may be combined to facilitate the simultaneous formation of reaction products and separation of these compounds from the reactor. This process principle is commonly known as reactive distillation when the reaction is a homogeneous liquid phase reaction. When the catalyst system exhibits no solubility in the solvent or reaction products, and is fixed in the reactor so that it does not exit the reactor with the reactor product, solvent and unreacted olefin, the process principle is commonly known as catalytic distillation.

According to a further aspect of the invention, there is provided a catalyst system, as described above, for the tetramerisation of olefins. The catalyst system may include a heteroatomic ligand as described above and a transition metal. The catalyst system may also include an activator as described above.

According to an even further aspect of the invention, there is provided a ligand, as described above, for a catalyst system, as described above, for the tetramerisation of olefins.

EXAMPLES OF PERFORMING THE INVENTION

The invention will now be described with reference to the following examples which are not in any way intended to limit the scope of the invention.

In the examples that follow all procedures were carried out under inert conditions, using pre-dried reagents.

Example 1: Ethylene tetramerisation reaction using Cr (III) acetylacetone, (4-methoxyphenyl)₂PN(methyl)P(4-methoxyphenyl)₂ and MAO

A solution of 30.0 mg of (4-methoxyphenyl)₂PN(methyl)P(4-methoxyphenyl)₂ (0.066 mmol) in 10 ml of toluene was added to a solution of 11.5 mg chromium (III) acetylacetone (0.033 mmol) in 10 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (80ml) and MAO (methylaluminoxane, 9.9 mmol) at 60°C. The pressure reactor was charged with ethylene after which the reactor temperature was maintained at 65°C, while the ethylene pressure was kept at 30 barg. Thorough mixing was ensured throughout by mixing speeds of 1100 RPM's using a gas entraining stirrer. The reaction was terminated after 30 minutes by discontinuing the ethylene feed to the reactor and cooling the reactor to below 10°C. After releasing the excess ethylene from the autoclave, the liquid contained in the autoclave was quenched with ethanol followed by 10% hydrochloric acid in water. Nonane was added as an internal standard for the analysis of the liquid phase by GC-FID. A small sample of the organic layer was dried over anhydrous sodium sulfate and then analysed by GC-FID. The remainder of the organic layer was filtered to isolate the solid wax/polymeric products. These solid products were dried overnight in an oven at 100°C and then weighed to yield 0.2254 g of polyethylene. The GC analyses indicated that the reaction mixture contained 39.54g oligomers. The product distribution of this example is summarised in Table 1.

Example 2: Ethylene tetramerisation reaction using Cr (III) acetylacetone, (4-methoxyphenyl)₂PN(methyl)P(4-methoxyphenyl)₂ and MAO

A solution of 30.0 mg of (4-methoxyphenyl)₂PN(methyl)P(4-methoxyphenyl)₂ (0.066 mmol) in 10 ml of toluene was added to a solution of 11.5 mg chromium

(III) acetylacetone (0.033 mmol) in 10 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (80ml) and MAO (methylaluminoxane, 9.9 mmol) at 40°C. The pressure reactor was charged with ethylene after which the reactor temperature was maintained at 45°C, while the ethylene pressure was kept at 45 barg. Thorough mixing was ensured throughout by mixing speeds of 1100 RPM's using a gas entraining stirrer. The reaction was terminated after 30 minutes by discontinuing the ethylene feed to the reactor and cooling the reactor to below 10°C. After releasing the excess ethylene from the autoclave, the liquid contained in the autoclave was quenched with ethanol followed by 10% hydrochloric acid in water. Nonane was added as an internal standard for the analysis of the liquid phase by GC-FID. A small sample of the organic layer was dried over anhydrous sodium sulfate and then analysed by GC-FID. The remainder of the organic layer was filtered to isolate the solid wax/polymeric products. These solid products were dried overnight in an oven at 100°C and then weighed to yield 5.4416 g of polyethylene. The GC analyses indicated that the reaction mixture contained 41.27g oligomers. The product distribution of this example is summarised in Table 1.

Example 3: Ethylene tetramerisation reaction using Cr (III) acetylacetone, (3-methoxyphenyl)₂PN(methyl)P(3-methoxyphenyl)₂ and MAO

A solution of 30.0 mg of (3-methoxyphenyl)₂PN(methyl)P(3-methoxyphenyl)₂ (0.066 mmol) in 10 ml of toluene was added to a solution of 11.5 mg chromium (III) acetylacetone (0.033 mmol) in 10 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (80ml) and MAO (methylaluminoxane, 9.9 mmol) at 60°C. The pressure reactor was charged with ethylene after which the reactor temperature was maintained at 65°C, while the ethylene pressure was kept at 30 barg. Thorough mixing was ensured throughout by mixing speeds of 1100 RPM's using a gas entraining stirrer. The reaction was terminated after 30 minutes by discontinuing the ethylene feed to

the reactor and cooling the reactor to below 10°C. After releasing the excess ethylene from the autoclave, the liquid contained in the autoclave was quenched with ethanol followed by 10% hydrochloric acid in water. Nonane was added as an internal standard for the analysis of the liquid phase by GC-FID. A small sample of the organic layer was dried over anhydrous sodium sulfate and then analysed by GC-FID. The remainder of the organic layer was filtered to isolate the solid wax/polymeric products. These solid products were dried overnight in an oven at 100°C and then weighed to yield 1.2269 g of polyethylene. The GC analyses indicated that the reaction mixture contained 9.71g oligomers. The product distribution of this example is summarised in Table 1.

Example 4: Ethylene tetramerisation reaction using Cr (III) acetylacetone, (3-methoxyphenyl)₂PN(methyl)P(3-methoxyphenyl)₂ and MAO

A solution of 30.0 mg of (3-methoxyphenyl)₂PN(methyl)P(3-methoxyphenyl)₂ (0.066 mmol) in 10 ml of toluene was added to a solution of 11.5 mg chromium (III) acetylacetone (0.033 mmol) in 10 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (80ml) and MAO (methylaluminoxane, 9.9 mmol) at 40°C. The pressure reactor was charged with ethylene after which the reactor temperature was maintained at 45°C, while the ethylene pressure was kept at 45 barg. Thorough mixing was ensured throughout by mixing speeds of 1100 RPM's using a gas entraining stirrer. The reaction was terminated after 30 minutes by discontinuing the ethylene feed to the reactor and cooling the reactor to below 10°C. After releasing the excess ethylene from the autoclave, the liquid contained in the autoclave was quenched with ethanol followed by 10% hydrochloric acid in water. Nonane was added as an internal standard for the analysis of the liquid phase by GC-FID. A small sample of the organic layer was dried over anhydrous sodium sulfate and then analysed by GC-FID. The remainder of the organic layer was filtered to isolate the solid wax/polymeric products. These solid products were dried overnight in an oven at 100°C and then weighed to yield 4.1301 g of polyethylene. The GC

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analyses indicated that the reaction mixture contained 17.70g oligomers. The product distribution of this example is summarised in Table 1.

Table 1: Ethylene tetramerisation runs: Examples 1- 4

| Example | Activity g prod./g Cr | Total Product g | Solids Wt % | Liquids Wt % | Liquid Product Distribution Wt % | | | | | 1- Octene in C ₈ Wt % |
|---------|--------------------------------|-----------------------|----------------|-----------------|-------------------------------------|----------------|----------------|-----------------|------------------|---|
| | | | | | C ₄ | C ₆ | C ₈ | C ₁₀ | C ₁₁₊ | |
| 1 | 23232 | 39.77 | 0.57 | 99.43 | 3.1 | 25.3 | 48.8 | 1.2 | 17.2 | 93.5 |
| 2 | 27292 | 46.72 | 11.65 | 88.35 | 1.1 | 18.9 | 43.4 | 2.2 | 31.2 | 91.2 |
| 3 | 6376 | 10.94 | 11.21 | 88.79 | 2.8 | 33.8 | 37.5 | 1.4 | 19.5 | 92.2 |
| 4 | 12724 | 21.83 | 18.92 | 81.08 | 2.0 | 19.5 | 26.7 | 1.7 | 46.6 | 89.7 |

DATED THIS 6TH DAY OF OCTOBER, 2003.

Perry
HAHN & HAHN INC.
 Agents for Applicant